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Wetlands as principal zones of methylmercury production in southern Louisiana and the Gulf of Mexico region

B.D. Hall [a,b,*], G.R. Aiken [c], D.P. Krabbenhoft [d], M. Marvin-DiPasquale [e], C.M. Swarzenski [f]

[a] Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, WI 53706, USA
[b] Department of Biology, University of Regina, 3737 Wascana Parkway, Regina, SK, S4S 0A2, Canada
[c] United States Geological Survey, 3215 Marine Street, Boulder, CO 80303, USA
[d] United States Geological Survey, 8505 Research Way, Middleton, WI 53562, USA
[e] United States Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, USA
[f] United States Geological Survey, Suite 120, 3535 S. Sherwood Forest Blvd., Baton Rouge, LA 70816, USA

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This study, which presents the results of a landscape scale examination of methylmercury and total mercury cycling in southern Louisiana, shows that freshwater, brackish, and marine wetlands are important sites of methylmercury production, which could lead to increased fish Hg concentrations in the Gulf of Mexico region.

Abstract

It is widely recognized that wetlands, especially those rich in organic matter and receiving appreciable atmospheric mercury (Hg) inputs, are important sites of methylmercury (MeHg) production. Extensive wetlands in the southeastern United States have many ecosystem attributes ideal for promoting high MeHg production rates; however, relatively few mercury cycling studies have been conducted in these environments. We conducted a landscape scale study examining Hg cycling in coastal Louisiana (USA) including four field trips conducted between August 2003 and May 2005. Sites were chosen to represent different ecosystem types, including: a large shallow eutrophic estuarine lake (Lake Pontchartrain), three rivers draining into the lake, a cypress-tupelo dominated freshwater swamp, and six emergent marshes ranging from a freshwater marsh dominated by *Panicum hemitomon* to a *Spartina alterniflora* dominated salt marsh close to the Gulf of Mexico. We measured MeHg and total Hg (THg) concentrations, and ancillary chemical characteristics, in whole and filtered surface water, and filtered porewater.

Overall, MeHg concentrations were greatest in surface water of freshwater wetlands and lowest in the profundal (non-vegetated) regions of the lake and river mainstems. Concentrations of THg and MeHg in filtered surface water were positively correlated with the highly reactive, aromatic (hydrophobic organic acid) fraction of dissolved organic carbon (DOC). These results suggest that DOC plays an important role in promoting the mobility, transport and bioavailability of inorganic Hg in these environments. Further, elevated porewater concentrations in marine and brackish wetlands suggest coastal wetlands along the Gulf Coast are key sites for MeHg production and may be a principal source of MeHg to foodwebs in the Gulf of Mexico.

Examining the relationships among MeHg, THg, and DOC across these multiple landscape types is a first step in evaluating possible links between key zones for Hg(II)-methylation and the bioaccumulation of mercury in the biota inhabiting the Gulf of Mexico region.

Keywords: Mercury; Methylmercury; Wetlands; Louisiana; Dissolved organic carbon; Sulphate

1. Introduction

Over the past 100 years, substantial increases in anthropogenic mercury (Hg) emissions have resulted in conditions whereby even the most remote locations are now Hg-contaminated (Fitzgerald et al., 1998; Mason and Sheu, 2002; Schroeder

* Corresponding author. Department of Biology, University of Regina, 3737 Wascana Parkway, Regina, SK, S4S 0A2, Canada. Tel.: +1 306 3372355; fax: +1 306 3372410.
E-mail address: britt.hall@uregina.ca (B.D. Hall).

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and Munthe, 1998). On a global basis, the major sources of Hg to the atmosphere are emissions from coal-fired energy production and waste incineration (Hylander and Meili, 2003; Pai et al., 2000). These fluxes are likely to increase as industrialization increases globally, especially in Asia.

Mercury contamination generally only becomes problematic when fallout from the atmosphere occurs on aquatic ecosystems, where the conversion of a small portion of the inorganic Hg(II) to MeHg can result in high levels of Hg in tissues of biota at the top of aquatic food webs (Hall et al., 2005; Mason et al., 2000; St. Louis et al., 1995; Swain et al., 1992). The methylation of Hg(II) is the most important transformation in the environmental Hg cycle because MeHg is a neurotoxin that is easily bioaccumulated by humans and wildlife that consume fish (Hightower and Moore, 2003; Wiener et al., 2003). Therefore, because atmospheric deposition is the principal Hg source to most settings, potentially unsafe levels of Hg in consumable game fish can occur anywhere conditions promote the methylation process. Mercury methylation is generally thought to be facilitated by sulphate reducing bacteria, which thrive in organic-rich, anaerobic sediments of many of aquatic systems (e.g., wetland soils, lake sediments) (Branfireun et al., 1999; Compeau and Bartha, 1984; Gilmour and Henry, 1991). Although a generalized understanding of MeHg production has been realized over the past decade or so, we still lack the ability to predict *a priori* what specific ecosystems, or specific regions may be more problematic than others.

It is widely recognized that *in situ* production of MeHg via microbial methylation is the main source of MeHg to most aquatic systems (Gilmour and Riedel, 1995; Pak and Bartha, 1998). Wetland sediments, in particular, possess many environmental factors that promote Hg(II) methylation and are recognized as ''hot spots'' for MeHg production (Branfireun et al., 1999; Gilmour et al., 1992; St. Louis et al., 1994). The amount of MeHg produced in an environment depends, in part, on factors that control microbial population growth or metabolic function (Gilmour and Henry, 1991; Winfrey and Rudd, 1990) and on the availability of Hg(II) for methylation (i.e. bioavailability). Important ecological factors include the rate of substrate supply for microbial growth, such as labile dissolved organic carbon (DOC) (Aiken et al., 2003; Hall et al., 2004) and SO_4/S^{-2} (Benoit et al., 1999), pH (Miskimmin et al., 1992; Regnell, 1994; Winfrey and Rudd, 1990), and temperature (Bodaly et al., 1993). Microbial MeHg production also requires Hg(II) capable of crossing cell membranes (Barkay et al., 1997; Kelly et al., 2003). This ''bioavailable'' Hg is likely highly reducible, reactive Hg(II), which may or may not be associated with other compounds, such as chloride (Barkay et al., 1998), sulphides (Benoit et al., 2001; Benoit et al., 1999), or either high- (Aiken et al., 2003; Barkay et al., 1997), or low-molecular weight organic compounds (Golding et al., 2002) that can comprise DOC in the environment.

To date, the majority of scientific understanding on these issues is derived from research on inland, freshwater systems. Conditions in coastal wetlands, estuaries, and salt marshes may also be favourable to the anaerobic bacteria that facilitate methylation (Benoit et al., 1998; Hammerschmidt and Fitzgerald, 2004; Lambertsson and Nilsson, 2006; Marvin-DiPasquale and Agee, 2003; Marvin-DiPasquale et al., 2003). With the presence of abundant wetlands and other ecosystem characteristics ideal for promoting elevated MeHg production, the Gulf Coast and southeastern Atlantic coast of the United States may be especially prone to Hg contaminated food webs. As well, this area is prone to substantial atmospheric deposition of Hg to the near-shore continental regions (Engle et al., in press). However, there is little information on Hg cycling in these systems. In addition, the proximity of these systems to the Gulf of Mexico, where high levels of Hg in commercial fish are common (Louisiana Department of Health and Hospitals, 2003), suggests that MeHg production in coastal wetlands may be transported to food webs in the Gulf of Mexico.

The objective for this study was to examine Hg and MeHg cycling in different habitats at the landscape scale in coastal Louisiana (USA). Specifically, we explored relations among Hg, MeHg, and DOC in different habitats typical of the Gulf of Mexico region, including large lakes, rivers, and both freshwater and saltwater influenced wetlands. The study included four field trips conducted between August 2003 and May 2005. We measured MeHg and total Hg (THg) concentrations, and ancillary chemical characteristics, in whole and filtered surface water, and filtered porewater. Habitats in the region that have a high potential to methylate Hg were identified. This work provides a description of Hg cycling in the region and is intended to act as an introduction to further work examining processes regulating the production and transport of MeHg in these habitats.

2. Site selection and sampling methods

2.1. Sample sites

Field sampling was conducted four times between August 2003 and May 2005 (Fig. 1). We sampled a wide range of habitat types in August 2003: a large shallow eutrophic estuarine lake (Lake Pontchartrain), the upper and lower reaches of three rivers draining into Lake Pontchartrain (Bayou Lacombe, the Tangipahoa, and the Tchefuncte), the lower reaches of two rivers in cypress-tupelo dominated forests (Blind River and Bedico Creek) and an estuarine marsh (Bayou Lacombe; Table 1).

On subsequent sampling trips (April and September 2004 and May 2005), we added a marine lake (Lake Borgne), a cypress-tupelo dominated wetland (Robert's Marsh), a brackish marsh with tidal influences from Lake Pontchartrain (Bayou Lacombe wetland), a *Panicum hemitomon* dominated freshwater marsh (Jean Lafitte Morone), a *Spartina patens* dominated wetland (Jean Lafitte Treasure Island), and three *Spartina alterniflora* salt marshes (the Rigolets and Lake Felicity and Lake Junop marshes; Fig. 1). Surface water samples from rivers and lakes were taken in mid-channel of rivers or in the open water regions of lakes. Wetlands were sampled ~1–400 m from the primary surface water channels

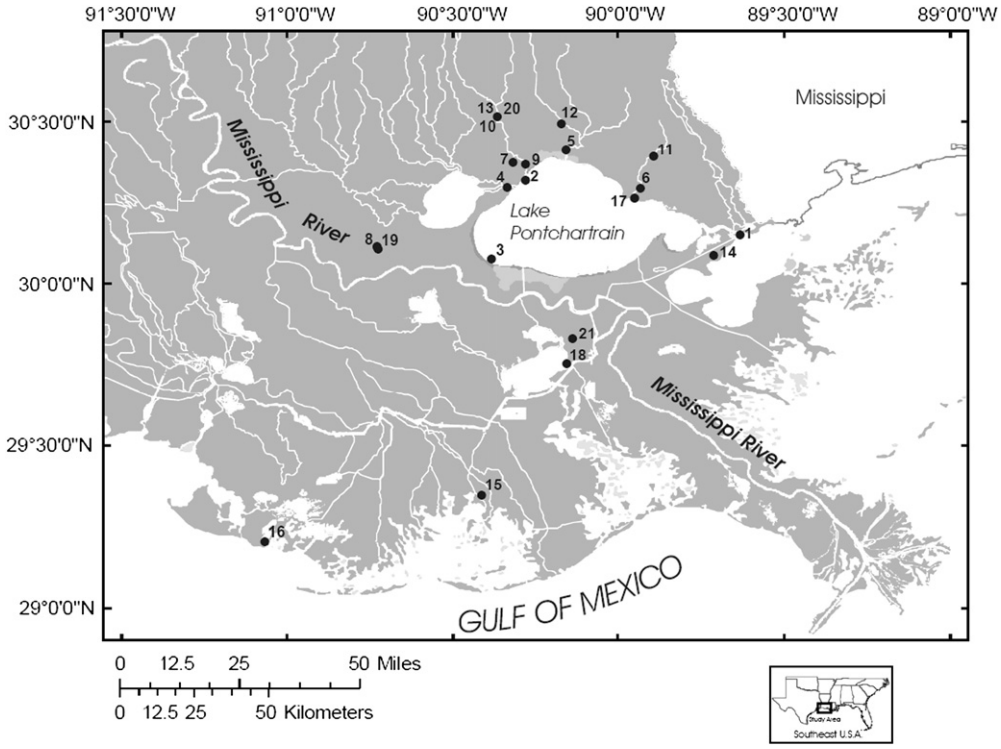

Fig. 1. Location of sites sampled throughout the study. Numbers refer to sites listed in Table 1.

associated with each wetland. At three of the wetlands (Blind River wetland, Bayou Lacombe wetland, and the Rigolets), we sampled surface and porewater at 4–6 stations along a ~100–400 m transect running from the main channel to the marsh interior. Total Hg, MeHg, and DOC concentrations at stations along each transect were similar to each other (unpublished data). Only one station was sampled at the other sites due to funding and time constraints.

2.2. Site classification

All sites were characterized based on water body types (lake, river, and wetland) and using specific conductivity as a proxy for salinity (Table 1). Three salinity categories were; freshwater to slightly brackish (<800–2000 μS cm^{-1}), moderately brackish to brackish (2000–15 000 μS cm^{-1}), and subsaline (>15 000 μS cm^{-1}). Wetland classification by salinity was based on salinity sub-classes of Stewart and Kantrud (1971) and water chemistry modifiers of Cowardin et al. (1979). Throughout this manuscript, freshwater and slightly brackish waters are referred to as ''freshwater'', moderately brackish and brackish waters as ''brackish'', and subsaline waters as ''marine''. There was one exception to the classification scheme. Although conductivity at Jean Lafitte Treasure Island (1940 μS cm^{-1}) was below the lower classification limit for conductivity in brackish wetlands (2000 μS cm^{-1}), the dominant vegetation (*Spartina patens*) and average chloride concentrations (typically 1500 mg mL^{-1}) were more typical of brackish wetlands. As well, long-term studies indicate that conductivity can range from 2000 to 8000 μS cm^{-1} (unpublished data, C. Swarzenski). Therefore, Jean Lafitte Treasure Island was classified as a brackish wetland. All data were averaged with equal weight within each of the habitat classifications.

3. Sampling and analytical methods

3.1. Mercury

Both surface water and porewater were sampled for THg (all forms of Hg) and MeHg were collected using trace-metal techniques (Olson and DeWild, 1999). Surface water samples were collected from open-water areas of the wetland channels beyond the fringe of vegetation. In shallow areas, hand grab samples were taken by wading into the open area and sampling into the current. In deep areas, hand-grab samples were taken off the bow of the boat while slowly moving forward. All surface water samples were taken in sterile fluoro-carbon polymer bottles and immediately placed on ice. At clean processing facilities, samples were filtered into Teflon bottles using 0.45 μm glass fibre filters and Teflon filter-holders. Filtered water was preserved using 6 N HCl to 1% volume to volume. Surface water filters loaded with particulate samples were immediately frozen on dry ice. Porewater samples were taken either using a Teflon sipper and battery-powered Geo-pump or by pumping water through Teflon lines from holes dug to water table depth. Porewater samples were filtered using an in-line Teflon glass fibre filter pack (0.45 μm). In order to prevent contamination of samples during sampling, all water samples were taken using clean hands/dirty hands sampling protocols (Olson et al., 1997; St. Louis et al., 1994).

Table 1
General characteristics and locations of sites sampled

Site	Dates sampled	Conductivity (μS cm^{-1})[a]	Salinity type[b]	Latitude, longitude[a]	Map no.[c]
Lakes sites					
Lake Borgne	September 2004	22000	Marine	ND	1
Lake Pontchartrain (Lumcon Platform)	August 2003	2224	Brackish	30°18.91′, 90°17.02′	2
Lake Pontchartrain (Bonnet Carre)	August 2003	4337	Brackish	30°04.43′, 90°23.00′	3
Pass Manchac	August 2003	ND	Brackish	30°17.78′, 90°20.21′	4
River sites					
Lower Tchefuncte River	August 2003	ND	Brackish	30°24.50′, 90°09.69′	5
Lower Bayou Lacombe	August 2003	6014	Brackish	30°17.52′, 89°55.95′	6
Lower Bayou Lacombe	April 2004	4000		ND	6
Lower Bayou Lacombe	September 2004	10000		ND	6
Bedico Creek	August 2003	308	Freshwater	30°22.28′, 90°19.19′	7
Blind River	August 2003	353	Freshwater	30°06.32′, 90°43.40′	8
Blind River	April 2004	720		ND	8
Blind River	September 2004	1100		ND	8
Lower Tangipahoa	August 2003	52	Freshwater	30°21.94′, 90°16.90′	9
Upper Tangipahoa	August 2003	ND	Freshwater	30°56.34′, 90°29.36′	10
Upper Tangipahoa	April 2004	52		30°30.24′, 90°21.72′	10
Upper Tangipahoa	September 2004	48		30°30.22′, 90°21.72′	10
Upper Bayou Lacombe	August 2003	351	Freshwater	30°23.57′, 89°53.62′	11
Upper Bayou Lacombe	September 2004	68		30°23.61′, 89°53.69′	11
Upper Tchefuncte River	August 2003	ND	Freshwater	30°29.54′, 90°10.37′	12
Skull Creek	April 2004	110	Freshwater	30°30.51′, 90°21.73′	13
Wetland sites					
Rigolets	September 2004	18875	Marine	30°08.90′, 89°38.05′	14
Felicity	May 2005	28900	Marine	29°20.91′, 90°24.88′	15
Junop	May 2005	17250	Marine	29°12.18′, 91°03.95′	16
Bayou Lacombe	April 2004	6940	Brackish	30°15.74′, 89°56.97′	17
Bayou Lacombe	September 2004	11923		30°15.73′, 89°56.98′	17
Jean Lafitte Treasure Island	May 2005	1940	Brackish	ND	18
Blind River	April 2004	583	Freshwater	30°06.51′, 90°43.38′	19
Blind River	September 2004	920		30°06.53′, 90°43.40′	19
Robert's Marsh	April 2004	84	Freshwater	30°30.44′, 90°21.79′	20
Jean Lafitte Morone	May 2005	901	Freshwater	29°49.79′, 90°8.41′	21

[a] ND represents no data. Salinity types for sites with no data were assigned based either on data existing for other time periods or on vegetation and location on landscape.
[b] Freshwater, 0–2000 μS cm^{-1}; brackish, 2000–12 000 μS cm^{-1}; marine, >12 000 μS cm^{-1}.
[c] Map no. corresponds to site location in Fig. 1.

Total Hg and MeHg analyses were performed on filtered surface water, suspended particulates collected on filters, and filtered porewater. All Hg samples were analyzed at the US Geologic Survey (USGS) Mercury Research Laboratory in Middleton, WI. Samples for MeHg were distilled, ethylated, and analyzed by cold-vapour atomic fluorescence spectrometry (CVAFS) (Bloom, 1989; Horvat et al., 1993; Liang et al., 1994). THg analysis by CVAFS after BrCl oxidation and $SnCl_2$ reduction followed EPA Method 1631 (USEPA, 2002). Detection limits for both MeHg and THg analysis were between 0.01 and 0.05 ng L^{-1}. Matrix spike recoveries for MeHg and THg were generally >80% and >90%, respectively.

3.2. Other parameters

Samples for DOC concentrations, specific UV absorbance (SUVA), hydrophobic organic acids (HPOA), pH, conductivity and major anions were taken concurrently with Hg samples. Samples were taken in polycarbonate bottles, filtered using either 0.45 glass fibre or Gelman AquaPrep 600 capsule filters, and shipped on ice to the USGS laboratory in Boulder, CO. Conductivity, pH, and major anion concentrations were analyzed in Boulder using standard methods (conductivity, Amber Science Model 2052 Meter; pH, Beckman Futura combination pH electrode; anions as in Fishman and Friedman (1989)). DOC measurements were made using the Pt-catalyzed persulphate wet oxidation method on an OI Analytical Model 700 TOC Analyzer (Aiken, 1992). Standard deviation for the DOC measurement was determined to be ±0.2 mg C L^{-1}. UV absorbance measurements at $\lambda = 254$ nm, a wavelength associated with the aromatic moieties in a sample (Chin et al., 1994) were made at room temperature on a Hewlett-Packard Model 8453 PhotoDiode array spectrophotometer utilizing a 1 cm path length quartz cell (standard deviation ±0.002). Specific ultraviolet absorbance (SUVA) was determined by dividing the UV absorbance measured at $\lambda = 254$ nm by the DOC concentration as described by Weishaar et al. (2003). SUVA values are reported in units of L mg C^{-1} cm^{-1}

and have a standard deviation of ±0.0015 L mg C^{-1} cm^{-1}. DOC in select whole water samples was fractionated using a modified version of the XAD-8/XAD-4 methods used to isolate organic matter from water samples (Aiken et al., 1992). In short, 1 L of a filtered sample, acidified to pH 1.85–1.95, was passed through a 20 mL glass column packed with Amberlite™ XAD-8 resin. The HPOA fraction of the DOC, also defined as "humic", was retained on the Amberlite™ XAD-8 resin and was recovered by back-eluting the column with 100 mL of 0.1 N sodium hydroxide solution. DOC and UV absorbance measurements were taken on the acidified HPOA fraction. SUVA values and % HPOA by mass balance were calculated.

4. Results and discussion

4.1. Total Hg, MeHg, and DOC concentrations

4.1.1. Surface waters

Total Hg and MeHg concentrations at the Morone site in Jean Lafitte National Park were significantly higher than other sites and were excluded from the averages (Table 2). The Morone site was unique in that there was water hyacinth covering the surface of the entire pond. Although many of the within site averages had high standard errors, this was not unexpected because of the diversity of habitat types sampled. Seasonal and inter-annual variability in physio-chemical parameters (such as temperature and hydroperiods) may also have contributed to high standard errors. Generally, average THg concentrations in surface water were similar among site categories (Table 2). Whole water THg concentrations (dissolved plus particulate) ranged from 2 ng L^{-1} in brackish lakes to over 5 ng L^{-1} in freshwater wetlands (Table 2). The majority of THg was present in the dissolved phase, with the exception of three marine-influenced ecosystems; marine lake, marine wetlands, and brackish wetlands, all of which had proportionally more THg attached to particles (Table 2).

Marine and brackish lakes had the lowest average whole water (dissolved plus particulate) MeHg concentrations (<0.1 ng L^{-1}), whereas brackish and freshwater wetlands had the highest concentrations (0.51 and 0.45 ng L^{-1}, respectively; Table 2). With the exception of marine wetlands, the majority of MeHg existed in the dissolved phase (Table 2).

DOC concentrations varied among the sites ranging from relatively high values associated with brackish rivers to the lowest values associated with marine lake samples. Marine lakes were most influenced by autochthonous generation of DOC and by waters, as well as DOC associated with the Gulf of Mexico (Table 3). The composition of the DOC between sites also varied as indicated by the measured SUVA values (Table 3), which may be a reliable indicator of the aromaticity of DOC (Weishaar et al., 2003). Based on the SUVA data, dissolved organic matter (DOM) in the freshwater wetlands and the brackish rivers was the most aromatic, suggesting that the plants and soils of the watershed were important sources of the organic matter in these systems (McKnight and Aiken, 1998). The DOM in marine lakes and marine wetlands was the least aromatic, consistent with microbial and marine sources of DOM. These waters also had the lowest amounts of the HPOA fraction, an estimate of the amount of humic material in a sample.

Average THg concentrations in porewater ranged from less than 2 ng L^{-1} to more than 5 ng L^{-1} and were similar to those in surface waters, with the exception of the porewater at the brackish wetland sites (5.6 ± 0.8 ng L^{-1}; Table 2). In the marine and brackish wetlands, average MeHg concentrations in porewaters were substantially greater than concentrations in corresponding surface waters (Table 2). Average MeHg concentrations at the freshwater wetlands were only slightly elevated over surface waters (0.49 ng L^{-1} and 0.31 ng L^{-1}, respectively), whereas there was no difference between

Table 2
Average methylmercury (MeHg) and mercury concentrations for water types based on salinity (surface water only)

	MeHg (ng L^{-1})		Total Hg (ng L^{-1})		Inorganic Hg (ng L^{-1})[a]	%MeHg	
	Dissolved	Particulate	Dissolved	Particulate		Whole water	Dissolved
Surface water							
Marine lakes	0.04	0.02	0.59	2.85	3.38	1.8	6.8
Marine wetlands	0.06 ± 0.02	0.08 ± 0.02	0.67 ± 0.06	1.92 ± 0.30	2.44 ± 0.32	6.4 ± 1.8	9.5 ± 2.8
Brackish lakes	0.04 ± 0	0.02 ± 0	1.16 ± 0.12	0.86 ± 0.17	1.97 ± 0.17	2.8 ± 0.2	3.5 ± 0.4
Brackish rivers	0.17 ± 0.10	0.05 ± 0.02	2.72 ± 0.82	1.00 ± 0.18	3.49 ± 0.90	5.3 ± 2.2	5.5 ± 2.1
Brackish wetlands	0.33 ± 0.15	0.18 ± 0.10	1.62 ± 0.28	4.00 ± 2.38	5.11 ± 2.42	11.9 ± 4.9	16.5 ± 6.3
Freshwater rivers	0.16 ± 0.04	0.05 ± 0.01	2.00 ± 0.27	1.04 ± 0.11	2.84 ± 0.27	6.6 ± 0.9	7.5 ± 1.1
Freshwater wetlands[b]	0.31 ± 0.06	0.14 ± 0.07	1.64 ± 0.11	0.84 ± 0.04	2.04 ± 0.08	17.7 ± 3.9	18.7 ± 2.3
Porewater							
Marine wetlands	1.02 ± 0.69	ND[c]	1.49 ± 0.54	ND	18.1 ± 4.5	ND	23.0 ± 4.5
Brackish wetlands	2.15 ± 0.97	ND	5.58 ± 0.82	ND	34.5 ± 13.4	ND	34.5 ± 12.5
Freshwater rivers	0.13 ± 0.06	ND	2.18 ± 0.42	ND	6.57 ± 2.9	ND	6.6 ± 2.9
Freshwater wetlands[b]	0.49 ± 0.18	ND	3.05 ± 0.85	ND	22.4 ± 11.2	ND	22.0 ± 11.2

[a] Concentrations of inorganic water are given for whole surface water and filtered porewater.
[b] MeHg, THg, and %MeHg were extremely high (whole water MeHg, 3.33 ng L^{-1}; THg, 6.89 ng L^{-1}; %MeHg, 84.7%) at the Jean Lafitte Morone site and were not included in averages.
[c] ND, no data.

Table 3
Average dissolved organic carbon (DOC), specific UV absorbance (SUVA), hydrophobic organic acid (HPOA), and inorganic anion concentrations for sample types based on salinity

	DOC (mg C L^{-1})	SUVA (L mg C^{-1} cm^{-1})	Amount HPOA (mg C L^{-1})	%HPOA	SO_4^{-2} (mg L^{-1})	Cl^- (mg L^{-1})
Surface water						
Marine lakes	4.9	2.6	1.9	39	1050	7340
Marine wetlands	7.2 ± 1.1	2.8 ± 0.1	2.9 ± 0.4	41 ± 1	909 ± 121	7222 ± 1068
Brackish lakes	14.8 ± 5.1	3.7 ± 0.3	3.2 ± 0.4	42 ± 7	95 ± 33	727 ± 242
Brackish rivers	30.2 ± 8.3	4.0 ± 0.3	7.3 ± 1.7	59 ± 2	63 ± 42	411 ± 345
Brackish wetlands	11.6 ± 3.1	3.9 ± 1.3	6.3 ± 1.9	52 ± 4	417 ± 276	3055 ± 1889
Freshwater rivers	7.5 ± 1.7	3.6 ± 0.1	3.9 ± 1.1	49 ± 2	10 ± 4	42 ± 23
Freshwater wetlands[a]	11.6 ± 4.8	4.0 ± 0.5	6.1 ± 2.9	50 ± 4	16 ± 11	122 ± 68
r^2 with dissolved MeHg	0.329	0.507	0.655	–	0.127	0.213
r^2 with dissolved THg	0.687	0.650	0.696	–	0.575	0.626
Porewater						
Marine wetlands	10.7 ± 1.5	ND[b]	ND	ND	ND	ND
Brackish wetlands	23.0 ± 12.5	ND	ND	ND	ND	ND
Freshwater rivers	6.5 ± 4.2	ND	ND	ND	ND	ND
Freshwater wetlands[a]	20.2 ± 1.3	ND	ND	ND	ND	ND

[a] Morone site data were not included in averages. See footnote to Table 2.
[b] ND, no data.

MeHg concentrations in porewater and surface water at the freshwater rivers (Table 2). When concentrations differed between porewater and surface waters, this suggests that there is an increased potential for diffusive flux of MeHg from the sediments to the overlying water in these habitats. Porewater MeHg concentrations were 2.5 and 2.9 times higher than surface water concentrations at the brackish and freshwater wetlands and 16.5 times higher at the marine wetland.

Average DOC concentrations in porewater ranged from 6.5 mg C L^{-1} in freshwater to about 23.0 mg C L^{-1} in brackish wetlands. In brackish and freshwater wetlands porewater DOC was slightly elevated compared to the other sites (Table 3).

4.2. Relationships between Hg and other limnological parameters

A strong positive relation was observed between DOC and dissolved THg concentrations in filtered surface water ($r^2 = 0.69$, $p = 0.02$; Fig. 2A); but a slightly stronger relation exists between the HPOA fraction of the DOC and THg ($r^2 = 0.70$, $p = 0.02$; data not plotted). Dissolved THg concentrations were also positively correlated with SUVA values ($r^2 = 0.65$; Table 3), an indication of the reactivity of the DOC. Dissolved THg was negatively correlated with sulphate and chloride concentrations ($r^2 = 0.58$ and 0.63 respectively; Table 3). There was no apparent relationship between dissolved MeHg concentrations and DOC, although sites with elevated MeHg concentrations tended to have elevated DOC (exceeding 10 mg C L^{-1}; Fig. 2B). The lack of relationship between MeHg and DOC is not surprising given the myriad of other environmental factors that can influence methylation rates. Although we did not observe a significant relationship between MeHg and DOC, there was a significant correlation between MeHg and the amount of HPOA ($r^2 = 0.66$, $p = 0.03$; Fig. 2C). MeHg concentrations were also positively correlated with SUVA ($r^2 = 0.51$; Table 3). There was no relationship between dissolved MeHg concentrations and sulphate or chloride concentrations ($r^2 = 0.13$ and 0.21, respectively; Table 3).

Previous studies have shown that high DOC concentrations can both inhibit and stimulate the bioavailability of Hg (Gorski, 2004). While there is ample evidence that Hg–DOC interactions can influence methylation (see review by Ravichandran, 2004), studies examining DOC controls on methylation and MeHg uptake have focused on three possible mechanisms: (1) factors reducing Hg(II) available for uptake and subsequent methylation by bacteria; (2) stimulation of microbial activity by added carbon and thus increased methylation; and, (3) the role of DOC as a competitive complex for dissolved MeHg and thereby limiting uptake by the food web. High levels of DOC concentrations have been shown to inhibit methylation by the formation of large DOC–Hg complexes that cannot cross microbial cell membranes (Barkay et al., 1997; Kelly et al., 2003; Miskimmin et al., 1992). As well, DOC can reduce bioavailable Hg by enhancing photochemical reduction of Hg(II) to Hg^0 (Ravichandran, 2004), again reducing the amount of Hg(II) available for methylation. Studies have also shown that DOC can stimulate methylation by providing an organic carbon energy source and thus stimulating microbial activity (see review by Ullrich et al., 2001). In addition, recent studies suggest another possible mechanism that would allow increased methylation in the presence of DOC. The strength of DOC–Hg binding constants have been shown to be greater than previously thought, and in the absence of sulphide, Hg will preferentially bind to DOC (Haitzer et al., 2002). Of perhaps greater significance are the results of laboratory studies that have demonstrated that the

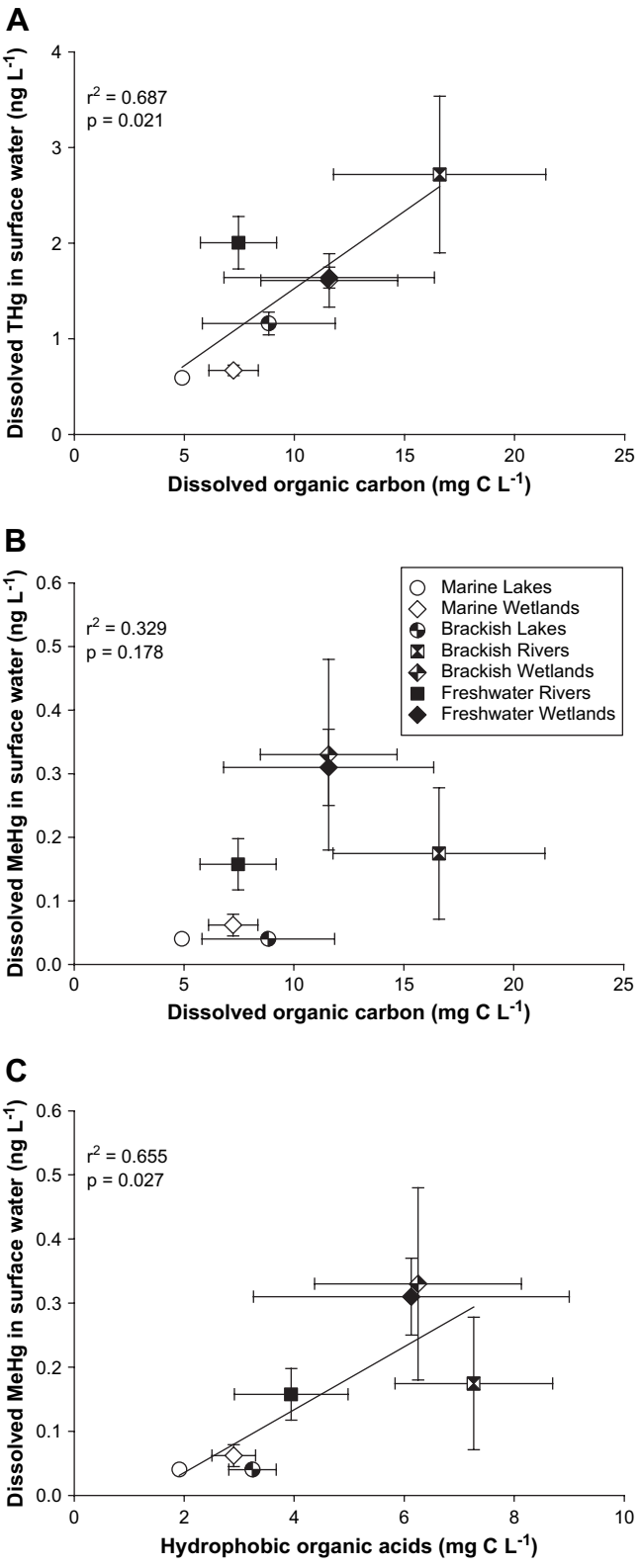

Fig. 2. Average concentrations of (A) total mercury (THg; ng L^{-1}) and (B) methylmercury (MeHg; ng L^{-1}) and dissolved organic carbon (mg C L^{-1}) in filtered surface water from sites classified by habitat type and salinity. (C) The relationship between average concentrations of MeHg (ng L^{-1}) and hydrophobic organic acids (mg C L^{-1}) in filtered surface water. Error bars in all panels represent standard errors. Legend in (B) applies to all panels.

presence of DOC can both enhance the solubility (Ravichandran et al., 1998) and inhibit the precipitation (Ravichandran et al., 1999) of insoluble Hg–S colloidal complexes. Whether due to strong complexation or colloidal stabilization, it is probable that DOC (and perhaps specifically HPOA) stabilizes THg in the dissolved phase, therefore increasing Hg(II) concentration (hence its bioavailability) at sites of methylation.

In the present study, we believe that the observed positive relations between (1) MeHg and HPOA, (2) THg and DOC and (3) THg and HPOA suggest that DOC (specifically the HPOA fraction of DOC) is a primary controlling factor in the production of MeHg, either by controlling the bioavailability of Hg or controlling Hg transport and concentrations. This control is not the same in all ecosystem types and is stronger when THg (rather than microbial activity) is a limiting factor for methylation. This positive relationship was also observed when examining inorganic Hg (calculated by subtraction of MeHg from THg; Table 2), which suggests that if DOC is stabilizing Hg in aqueous solution, it may occur independent of the source of Hg(II) to these environments.

4.3. Which ecosystem types are efficient methylators?

One of our objectives was to assess the ability of different ecosystem types to methylate Hg. Average MeHg concentrations were normalized by DOC concentrations within sites to allow assessment of the relative potential for MeHg production due to factors other than DOC. Habitats with high MeHg/DOC ratios would thus suggest enhanced methylation compared to those with low MeHg/DOC ratios, due to factors other than DOC itself. Applying this approach to the surface water data suggests that brackish and freshwater wetlands have a particularly high MeHg production potential (0.036 and 0.040 ng mg^{-1}, respectively), followed by freshwater rivers (0.027 ng mg^{-1}; Fig. 3). Conversely, marine lake habitats, brackish rivers and marine wetlands all exhibited a comparatively low MeHg/DOC ratio, suggesting a lower potential for MeHg production due to factors other than DOC. The trends in MeHg/DOC ratios largely paralleled the total amount of MeHg in whole water (dissolved plus particulate) giving credence to this approach.

Comparisons of methylation efficiency in different wetland types are complicated due to significant hydrological differences that exist among the sampled sub-ecosystems: freshwater-to-marine. Freshwater rivers that have high hydrological connectivity to wetlands may receive THg, MeHg, and DOC from wetlands. Freshwater wetlands in coastal Louisiana are driven by seasonal (spring and summer) hydro periods, whereas coastal marine wetlands are influenced by a shorter hydrologic periodicity (daily tidal cycles). Brackish wetlands undergo wet-dry cycles that characterize tidally influenced systems. In principle, the high variability of hydrologic cycles in brackish, and to a lesser degree freshwater, wetlands may result in unusually high rates of MeHg production. Seasonal differences in temperature may also impact MeHg production since methylation is a microbial process dependent on temperatures optimal for bacterial growth. Our samples were taken in

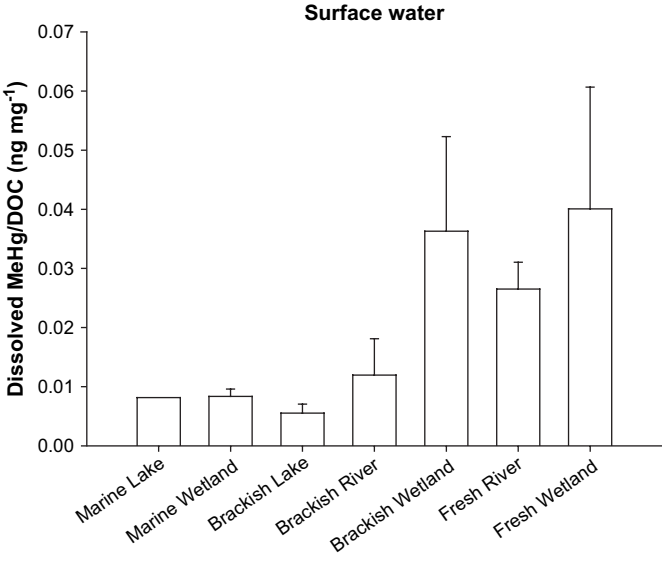

Fig. 3. Average methylmercury (MeHg) concentrations normalized to dissolved organic carbon (DOC) concentrations in filtered surface water. Error bars represent standard errors.

the spring, late summer, and fall seasons, and we would expect to see lower MeHg production in the cooler winter months.

During frequent water-level oscillations, anoxic wetland sediments, and similarly inundated soils, are exposed to oxygen, thereby oxidizing a portion of the reduced sulphur pool (mostly organic sulphur and sulphides) in sediments to SO_4^{-2}, which in turn can elevate MeHg production by stimulating sulphate reducing bacteria (Devito and Hill, 1999; Eimers et al., 2003). Similarly, re-wetting of oxidized substrates can increase the amount of labile DOC and other nutrients in a system, which can also promote microbial activity (Austin et al., 2004; Lundquist et al., 1999) and Hg methylation. Finally, oxidation of reduced sulphur and increased decomposition of organic matter may decrease pH once wetlands are re-flooded (Laudon et al., 2004). Studies have shown that decreased pH can stimulate methylation (Miskimmin et al., 1992; Xun et al., 1987), perhaps by increasing the activity of bioavailable Hg(II) (Kelly et al., 2003; Winfrey and Rudd, 1990). This may permit, as shown in wet–dry experiments in the Everglades (Krabbenhoft and Fink, 2000), the establishment of alternating oxic and anoxic conditions in the surface sediments where methylation is likely to be occurring, and thus stimulating methylation. As well, periodic tidal renewal in brackish wetlands may prevent the accumulation of dissolved sulphide (S^{-2}), which has been shown to inhibit methylation (Benoit et al., 1999).

4.4. Why are MeHg concentrations low in the marine wetland surface waters, but higher in marine porewaters?

Low surface water MeHg concentrations, as well as low MeHg/DOC ratios, at the marine wetland were surprising because many studies have shown that wetlands tend to be "hot spots" for Hg methylation. However, elevated porewater MeHg concentrations observed at the marine wetland (Table 3) suggest that despite low surface water concentrations, marine wetlands may be important sites of methylation. The moderate to high proportion of dissolved THg existing as dissolved MeHg (%MeHg $= 23.0 \pm 4.5$) in porewater also suggests that marine wetlands are active sites of methylation (Table 2). Sites with elevated fractions of the total Hg pool as MeHg are often indicative of sites of active methylation (Kelly et al., 1995; Rudd, 1995). Average %MeHg values in both surface and porewaters ranged from 3.5% in brackish lake surface water to 30% in brackish wetland porewater (Table 2). Freshwater wetlands had elevated %MeHg in both surface and porewaters, whereas %MeHg in marine wetlands was only high in the porewaters. It is likely that the majority of methylation in these systems occurs in the sediment and associated porewaters. Fluxes of MeHg from sediments to overlying water will occur at different rates in different ecosystem types. In the freshwater rivers and wetlands, MeHg concentrations in the surface and porewaters were close to equilibrium (Fig. 4A). In the marine and brackish wetlands, there was the potential for a net flux of MeHg from the porewaters to the overlying waters, further evidence that these systems were important methylators. The surface and porewater data also suggest that all types of wetland sediment export THg to surface waters and only freshwater wetlands sediments are sources of DOC (Fig. 4B and C). This data shows that using surface water concentrations to predict MeHg production may underestimate the potential of a system to methylate.

There are a number of possibilities that might explain lower than expected MeHg concentrations in surface waters in marine wetlands. One explanation may be dilution of MeHg in surface waters with tidal waters from the Gulf of Mexico. However, since the average DOC concentrations did not differ significantly between surface and porewaters (Table 2), MeHg would have to be diluted preferentially over DOC. Another explanation may be that marine wetlands offer environments that are more conducive to the removal of MeHg, via photoreduction or sorption. Environments with higher ionic strength favour stronger partitioning to the particulate phase (as shown in data from this study in Table 2), as well as the aggregation of DOM to colloidal-sized molecules or precipitation. If MeHg in marine wetlands is associated with HPOA in DOC, then the removal of DOC due to ionic precipitation would result in a shift from dissolved to particulate MeHg, increasing sedimentation of MeHg out of the water column. Differences in the ratio of dissolved to particulate THg in marine lakes and wetlands, and to MeHg in marine wetlands, support this explanation.

Porewater or sediment data are an important indication of methylating potential. Unfortunately, no porewater data was collected from brackish rivers, marine lakes, or brackish lakes for this study. Preliminary studies examining sediment MeHg and THg concentrations, as well as additional measurements of sediment Hg(II)-methylation rates via ^{203}Hg(II) radiotracer (unpublished data pending) confirm the current findings that wetlands in the coastal region of Louisiana are important sites of MeHg production.

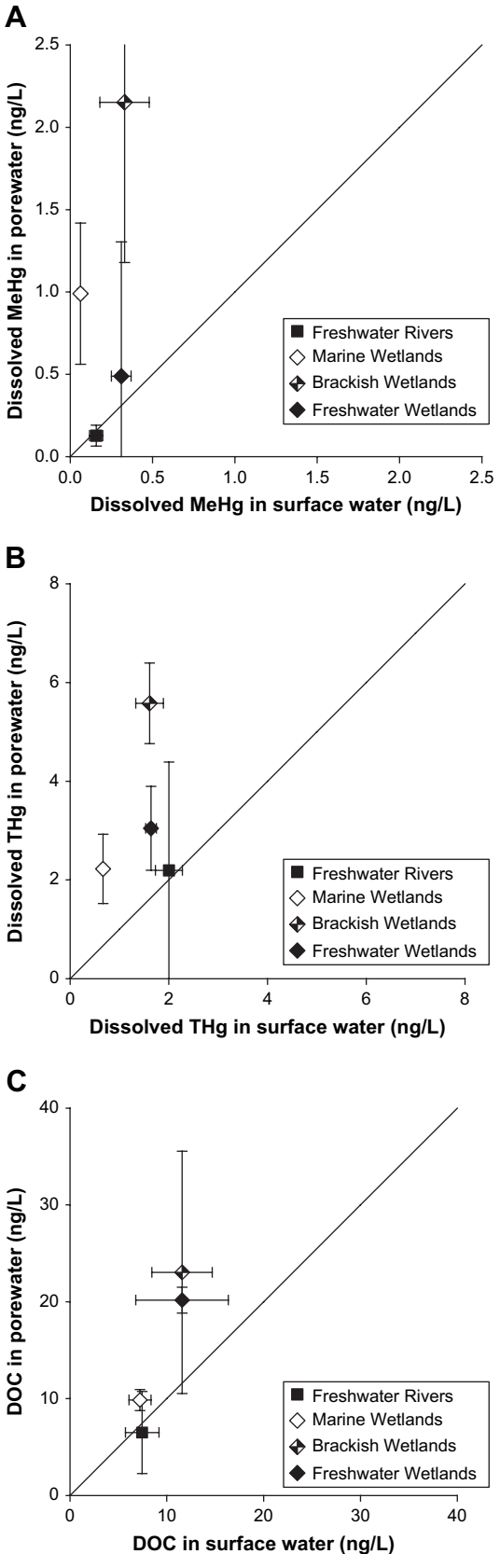

Fig. 4. Average concentrations of (A) methylmercury (MeHg), (B) total mercury (THg), and (C) dissolved organic carbon (DOC) in filtered surface waters (*X* axis) and filtered porewaters (*Y* axis). The reference line represents a 1:1 ratio. Data points above the line represent sites that have a flux from porewaters to surface waters. Error bars represent standard errors.

5. Summary

Near-coastal aquatic systems including rivers, estuaries and wetlands may be critical zones for Hg cycling and exert strong influences on near-shore marine foodwebs. However, it is unclear how coastal systems differ from freshwater environments in the complex biogeochemical interactions between Hg and DOC that influence the microbial production of MeHg. Therefore, Hg cycling models developed for freshwater systems may be inadequate in systems with increasing salinity. Although our study did not address temporal variability due to one time sampling at many sites, we have reported the results of a study designed to determine differences in Hg and MeHg concentrations in near coastal environments that receive similar atmospheric inputs of Hg. For a variety of surface water sites in Southern Louisiana in the Lake Pontchartrain region, THg concentrations (dissolved plus particulate) in surface water samples were very similar regardless of sample location, salinity or DOC concentration, perhaps suggesting similar sources in all systems. However, the distribution of Hg between dissolved and particulate phases for the marine samples strongly favoured particulate Hg, perhaps resulting from greater salinity and lower amounts of reactive DOC in the form of HPOA fraction. Differences in ionic strength may also account for stronger partitioning of THg to particles.

In contrast to THg, MeHg concentrations in surface waters were appreciably greater in freshwater and brackish wetlands, sites that were anticipated to support microbial methylation of Hg, and lowest in marine wetlands and brackish and marine open water systems. In all cases for the wetlands, including the marine wetlands, sediment porewaters contained greater concentrations of MeHg than river sediment samples suggesting that these marine wetlands were important sources of MeHg in this region. Despite low concentrations of MeHg in freshwater river sediments, river surface waters were found to have concentrations of MeHg intermediate between those found in surface waters from freshwater and brackish wetlands and those in the brackish and marine open water systems, possibly reflecting the influence of riparian wetlands on the chemistry of these rivers. The transport of MeHg from wetlands to open water systems is controlled, in part, by DOC quality and quantity, which, in turn, is based on watershed type. We suspect that the transport of Hg will impact on Hg(II) bioavailability to methylating bacteria, subsequent MeHg production and bioaccumulation, in these systems.

In recent years it has become apparent that although there has been a growing understanding of Hg cycling, MeHg production and bioaccumulation in freshwater systems, a similar general understanding for marine systems is not available. This lack of scientific understanding is even more important given the predominance of MeHg exposure to humans that occurs through the consumption of marine fish as opposed to freshwater fish. For important fisheries like the Gulf of Mexico, no published study can definitively point to a MeHg source that can explain the high levels of Hg in pelagic food webs. One possible MeHg source is food web connections to

sites of elevated MeHg production, such as the coastal wetland presented here. Further research on MeHg production in coastal settings and transfer to marine food webs is needed before such conclusions can be reached.

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